SOCCOM float deployments from Polarstern ANTXXX_2 PS89

2 February 2015

2 December 2014 – 1 February 2015
Cape Town to Cape Town (‚Goodhope line')
Chief Scientist: Olaf Boebel, Alfred Wegener Institut
Ship: Polarstern
Cruise identifier: ANTXXX_2 PS89
SOCCOM cruise identifier: 06AQ20141202

Float profile data available online: http://soccom.princeton.edu/soccomviz.php

The following text is excerpted from the complete AWI PS89 cruise report.

3.1.2 Biogeochemical Argo-type floats and nutrient measurements for SOCCOM (Southern Ocean Carbon and Climate Observations and Modelling)

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Objectives

The Southern Ocean surrounding Antarctica is the primary window through which the intermediate, deep, and bottom waters of the ocean interact with the surface and thus the atmosphere. In the past 20 years, observational analyses and model simulations have transformed understanding of the Southern Ocean, suggesting that the ocean south of 30°S, occupying just 30% of the total surface ocean area, has a profound influence on the Earth's climate and ecosystems. Prior results suggest that:

- the Southern Ocean accounts for up to half of the annual oceanic uptake of anthropogenic carbon dioxide from the atmosphere;
- vertical exchange in the Southern Ocean supplies nutrients that fertilize up to three-quarters of the biological production in the global ocean north of 30°S;
- the Southern Ocean accounts for about 75% ± 22% of the excess heat that is transferred from the atmosphere into the ocean each year; and
- Southern Ocean winds and buoyancy fluxes are the principal source of energy for driving the global large-scale deep meridional overturning circulation.

Model studies also project that changes in the Southern Ocean will have profound influence on future climate trends, with corresponding alteration of the ocean carbon cycle, heat uptake, and ecosystems. Projections include:

- due to ocean acidification, the Southern Ocean south of ~60°S will become undersaturated with respect to aragonite (a form of calcium carbonate) by ~2030 with a potentially large impact on calcifying organisms and Antarctic ecosystems; and
- the vertical exchange of deep and surface waters may either increase as winds over the Southern Ocean increase, or decrease as higher rainfall results in more stratification. More vertical exchange would be expected to result in more anthropogenic carbon uptake

from the atmosphere, but less storage of carbon through biological cycling, while its impact on heat uptake depends on whether it brings anomalously warm or cold waters to the ocean surface.

The SOCCOM (Southern Ocean Carbon and Climate Observations and Modelling) project is implementing sustained observations of the carbon cycle, together with mesoscale eddying models linked to the observations. 180 to 200 autonomous profiling floats with biogeochemical sensors (oxygen, nitrate, pH and optical sensors in addition to temperature/salinity) and sea-ice avoidance software are being deployed throughout the Southern Ocean over a period of six years. These will extend current seasonally limited observations of biogeochemical properties into nearly continuous coverage in time, with horizontal spatial coverage over the entire Southern Ocean and vertical coverage to 2000 m. These float deployments must take place from research ships with CTD/rosette sampling in order to collect water samples (to be analyzed for oxygen, nutrients, pH, alkalinity, HPLC, POC) for float profile calibration, and to collect in situ fluorescence and transmissometer profiles, also for float calibration. The first set of 6 prototype floats with this configuration of biogeochemical sensors was deployed in the Ross Sea and southern South Pacific in March-April, 2014 from GO-SHIP section P16S on the *RV Nathaniel B. Palmer*; the floats are operating well, with data reported in near real-time and publicly available from http://soccom.princeton.edu/soccomviz.php. The pH sensor technology, which was developed recently, is proving to be very robust. The T/S data are part of the Argo float data set.

All SOCCOM floats and calibration measurements, with the exception of the optical measurements, are supported by the U.S. National Science Foundation Polar Programs. Optical measurements instrumentation on the floats and HPLC/POC calibrations are supported by U.S. NASA.

The 12 floats deployed from *Polarstern PS89* are the first large-scale SOCCOM deployment, and are the first of our international collaborations. These floats will contribute to the international Southern Ocean Observing System (SOOS), and the Argo database.

Work at sea

(1) Profiling floats

Twelve SOCCOM floats were deployed according to Table 3.1 and Figure 3.1. All of these Argo-equivalent floats were equipped with state-of-the-art biogeochemical instrumentation. All but two have sea ice-avoidance software. All but three have pH sensors. Eight were Apex floats built at U. Washington from components purchased from Teledyne/Webb. Four were Navis floats from Sea-Bird Electronics (SBE), and are prototypes for SBE's new biogeochemical float program. Details of each float's capabilities are provided in Table 3.2.

PS89 deployments were carried out by Dan Schuller (SIO Oceanographic Data Facility) and Hannah Zanowski (Princeton U. graduate student), at the conclusion of the CTD/rosette cast.

As of 28 January, 2015, all 12 floats have been deployed, and are reporting good profiles, with the exceptions of 9125 and 9260 which have not yet reported, and of the pH sensor on float 0508, which failed on deployment. Several have already encountered sea ice but then successfully re-emerged, with resulting programmed delays in profile reporting. The first 8 floats were deployed along the Greenwich meridian, with locations chosen to sample each major oceanographic regime, based on previous hydrographic sections, and also tracer release and particle release numerical experiments in the Southern Ocean State Estimate (SOSE at SIO; M. Mazloff and J. Wang) and in the Hycom model (RSMAS U. Miami; I. Kamenkovich). The last 4 floats were intended for deployment across the Weddell Sea, but were released at the specified locations when it was decided that the Polarstern would return directly to Cape Town. The first two of this group were released far to the south in hopes that they would travel westward into the Weddell Sea. The third was released to increase density of the array and to supplement this region with a pH sensor. The fourth was released at the latitude of float 0508 to provide pH measurements in the polar frontal zone.

Table 3.1: SOCCOM PS89 float deployment details

Float ID	Argo identifier	Latitude Longitude	Sensors	Station #	Deployment date	Deployment time
0037 Navis	5904480	39° 13.9' S 11° 20.3' E	ONF	2-1	5-12-2014	0350Z
9313 Apex	5904474	44° 39.5' S 07° 05.6' E	ONFp	5-1	7-12-2014	0554Z
0508 Navis	5904481	49° 03.2' S 02° 52.1' E	IONFp*	8-1	9-12-2014	0100Z
9096 Apex	5904469	53° 31.0' S 00° 00.2' E	IONFp	12-2	10-12-2014	2234Z
0509 Navis	5904482	56° 55.8' S 00° 00.9' E	IONFp	16-1	12-12-2014	1100Z
7652 Apex	5904467	59° 59.0' S 00° 00.0' E	IONF	21-1	14-12-2014	0505Z
0511 Navis	5904483	64° 59.7' S 00° 00.1' E	IONFp	28-1	18-12-2014	0255Z
9094 Apex	5904471	66° 58.7' S 00° 00.6' W	IONFp	31-1	20-12-2014	0246Z
9275 Apex	5904472	67° 40.0' S 01° 45.2' W	IONFp	73-1	18-1-2015	0611Z
9099 Apex	5904468	66° 01.5' S 00° 02.0' E	IONFp	78-1	19-1-2015	0739Z
9125 Apex	5904397	61° 00.2' S 00° 00.1' W	IONFp	81-1	21-1-2015	1436Z
9260 Apex	5904473	49° 00.1' S 12° 56.1' E	IONFp	82-2	27-1-2015	1708Z

I = ice enabled; O = oxygen sensor; N = nitrate sensor; F = FLbb; p = pH
**pH sensor failed on deployment*

Table 3.2: SOCCOM PS89 float specifications

FLOAT NUMBER	TYPE(1)	MAX. DEPTH	O_2(2)	NO_3(3)	pH	OPTICS(4)	ICE CAPABLE(5)
7652	APEX	1750	✓	✓		✓	✓
9094	APEX	1750	✓	✓	✓	✓	✓
9096	APEX	1750	✓	✓	✓	✓	✓
9099	APEX	1750	✓	✓	✓	✓	✓
9125	APEX	1750	✓	✓	✓	✓	✓
9260	APEX	1750	✓	✓	✓	✓	✓
9275	APEX	1750	✓	✓	✓	✓	✓
9313	APEX	1750	✓	✓	✓	✓	
0037	Navis	2000	✓	✓		✓	
0509	Navis	2000	✓	✓	✓	✓	✓
0511	Navis	2000	✓	✓	✓	✓	✓
0508	Navis	2000	✓	✓	✓	✓	✓

Notes:

(1) APEX denotes floats built at UW from components purchased from Teledyne/Webb; Navis denotes floats purchased by UW in ready-to-deploy condition from SBE.

(2) O_2 sensor on APEX floats is Aanderaa 4330; on Navis floats it is SBE-63.

(3) NO_3 sensor on APEX floats is MBARI/ISUS; on Navis floats it is Satlantic/SUNA.

(4) OPTICS denotes WetLabs FLBB fluorometer and backscatter capability on APEX floats; on Navis floats, the optical sensor is ECO-MCOMC and includes a CDOM fluorometer in addition to chlorophyll fluorometer and backscattering.

(5) Ice capability is from field-tested softward developed at UW on APEX floats; on Navis floats it is from contributed software developed at UW but being tested in the field for the first time from this Polarstern set of float deployments.

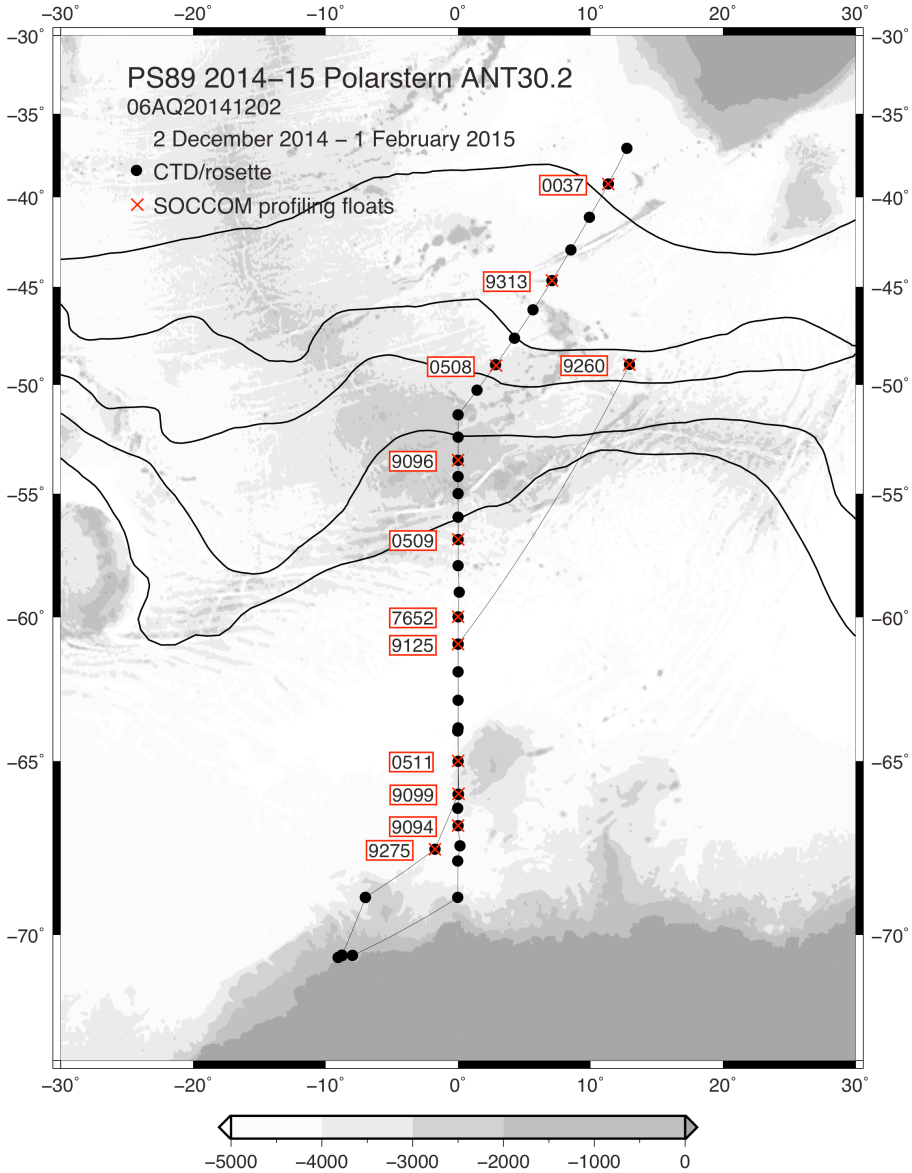

Figure 3.1. SOCCOM float deployments from Polarstern ANT30.2 (PS89) (red box labeling) with PS89 CTD stations (2 December 2014 – 1 February 2015). Light curves are the standard Orsi et al. (1995) fronts (subtropical, subantarctic, polar and southern boundary, from north to south).

(2) CTD/Rosette Sampling

CTD casts were completed at each SOCCOM float deployment location for a total of 12 profiles. Full water column bottle samples were taken by SIO-ODF for pH, alkalinity, nutrients, HPLC and POC at each station. ULPGC sampled and analysed water samples for oxygen and DIC, while AWI sampled and analysed water samples for salinity at these locations.

As SOCCOM's reciprocal contribution to the overall PS89 cruise, SIO-ODF collected and analyzed nutrient samples on board on all of the CTD/rosette stations (NSF funding). pH and alkalinity samples are being shipped to Andrew Dickson's laboratory at SIO (NSF funding). HPLC and POC samples are being shipped to Emmanuel Boss at U. Maine (NASA funding).

(3) Nutrients

Summary

1130 samples from SOCCOM and other CTD casts were analysed for nutrients. The cruise started with new pump tubes and they were changed once during the cruise, after *station 36-1*. Two sets of Primary/Secondary standards were made up over the course of the cruise. The cadmium column efficiency was checked periodically and was greater than 98%.

Equipment and Techniques

Nutrient analyses (phosphate, silicate, nitrate+nitrite, and nitrite) were performed on a Seal Analytical continuous-flow AutoAnalyzer 3 (AA3). The methods used are described by Gordon et al (1992) Hager et al. (1968), and Atlas et al. (1971). Details of modification of analytical methods used in this cruise are also compatible with the methods described in the nutrient section of the GO-SHIP repeat hydrography manual (Hydes et al., 2010)

Nitrate/Nitrite Analysis:

A modification of the Armstrong et al. (1967) procedure was used for the analysis of nitrate and nitrite. For nitrate analysis, a seawater sample was passed through a cadmium column where the nitrate was reduced to nitrite. This nitrite was then diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine to form a red dye. The sample was then passed through a 10mm flowcell and absorbance measured at 540nm. The procedure was the same for the nitrite analysis but without the cadmium column.

REAGENTS

Sulfanilamide

Dissolve 10g sulfamilamide in 1.2N HCl and bring to 1 liter volume. Add 2 drops of 40% surfynol 465/485 surfactant.

Store at room temperature in a dark poly bottle.

Note: 40% Surfynol 465/485 is 20% 465 plus 20% 485 in DIW.

N-(1-Naphthyl)-ethylenediamine dihydrochloride (N-1-N)

Dissolve 1g N-1-N in DIW, bring to 1 liter volume. Add 2 drops 40% surfynol 465/485 surfactant.

Store at room temperature in a dark poly bottle. Discard if the solution turns dark reddish brown.

Imidazole Buffer

Dissolve 13.6g imidazole in ~3.8 liters DIW. Stir for at least 30 minutes to completely dissolve. Add 60 ml of $CuSO_4$ + NH_4Cl mix (see below). Add 4 drops 40% Surfynol 465/485 surfactant. Let sit overnight before proceeding

Using a calibrated pH meter, adjust to pH of 7.83-7.85 with 10% (1.2N) HCl (about 10 ml of acid, depending on exact strength). Bring final solution to 4L with DIW.

Store at room temperature.

NH_4Cl + $CuSO_4$ mix:

Dissolve 2g cupric sulfate in DIW, bring to 100 m1 volume (2%)

Dissolve 250g ammonium chloride in DIW, bring to l liter volume.

Add 5ml of 2% $CuSO_4$ solution to this NH_4Cl stock. This should last many months.

Phosphate Analysis:
Ortho-Phosphate was analyzed using a modification of the Bernhardt and Wilhelms (1967) method. Acidified ammonium molybdate was added to a seawater sample to produce phosphomolybdic acid, which was then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The sample was passed through a 10mm flowcell and absorbance measured at 820nm (880nm after station 10, see section on analytical problems for details).

REAGENTS

Ammonium Molybdate
H2SO4 sol'n:
Pour 420 ml of DIW into a 2 liter Ehrlenmeyer flask or beaker, place this flask or beaker into an ice bath. SLOWLY add 330 ml of conc H2SO4.
This solution gets VERY HOT!! Cool in the ice bath. Make up as much as necessary in the above proportions.

Dissolve 27g ammonium molybdate in 250ml of DIW. Bring to 1 liter volume with the cooled sulfuric acid sol'n. Add 3 drops of 15% DDS surfactant. Store in a dark poly bottle.

Dihydrazine Sulfate
Dissolve 6.4g dihydazine sulfate in DIW, bring to 1 liter volume and refrigerate.

Silicate Analysis:
Silicate was analyzed using the basic method of Armstrong et al. (1967). Acidified ammonium molybdate was added to a seawater sample to produce silicomolybdic acid which was then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. The sample was passed through a 10mm flowcell and measured at 660nm.

REAGENTS

Tartaric Acid
Dissolve 200g tartaric acid in DW and bring to 1 liter volume. Store at room temperature in a poly bottle.

Ammonium Molybdate
Dissolve 10.8g Ammonium Molybdate Tetrahydrate in 1000ml dilute H2SO4*.
*(Dilute H2SO4 = 2.8ml conc H2SO4 or 6.4ml of H2SO4 diluted for PO4 moly per liter DW) (dissolve powder, then add H2SO4)
Add 3-5 drops 15% SDS surfactant per liter of solution.

Stannous Chloride
stock: (as needed)
Dissolve 40g of stannous chloride in 100 ml 5N HCl. Refrigerate in a poly bottle.

NOTE:
Minimize oxygen introduction by swirling rather than shaking the solution. Discard if a white solution (oxychloride) forms.

working: (every 24 hours)
Bring 5 ml of stannous chloride stock to 200 ml final volume with 1.2N HCl. Make up daily - refrigerate when not in use in a dark poly bottle.

Sampling:

Nutrient samples were drawn into 30 mL polypropylene screw-capped centrifuge tubes. The tubes and caps were cleaned with 10% HCI and rinsed 3 times with sample before filling. Samples were analyzed within 12 hours after sample collection, allowing sufficient time for all samples to reach room temperature. The centrifuge tubes fit directly onto the sampler.

Data collection and processing:

Data collection and processing was done with the software (ACCE ver 6.07) provided with the instrument from Seal Analytical. After each run, the charts were reviewed for any problems during the run, any blank was subtracted, and final concentrations (micro moles/liter) were calculated, based on a linear curve fit. Once the run was reviewed and concentrations calculated a text file was created. That text file was reviewed for possible problems and then converted to another text file with only sample identifiers and nutrient concentrations for merging with other bottle data.

Standards and Glassware calibration:

Primary standards for silicate (Na2SiF6), nitrate (KNO3), nitrite (NaNO2), and phosphate (KH2PO4) were obtained from Johnson Matthey Chemical Co. and/or Fisher Scientific. The supplier reports purities of >98%, 99.999%, 97%, and 99.999 respectively.
All glass volumetric flasks and pipettes were gravimetrically calibrated prior to the cruise. The primary standards were dried and weighed out to 0.1mg prior to the cruise. The exact weight was noted for future reference. When primary standards were made, the flask volume at 20C, the weight of the powder, and the temperature of the solution were used to buoyancy-correct the weight, calculate the exact concentration of the solution, and determine how much of the primary was needed for the desired concentrations of secondary standard. Primary and secondary standards were made up twice during the cruise. The new standards were compared to the old before use.

All the reagent solutions, primary and secondary standards were made with fresh distilled deionized water (DIW).

Standardizations were performed at the beginning of each group of analyses with working standards prepared prior to each run from a secondary. Working standards were made up in low nutrient seawater (LNSW). LNSW was collected off shore of coastal California and treated in the lab. The water was first filtered through a 0.45 micron filter then re-circulated for ~8 hours through a 0.2 micron filter, passed a UV lamp and through a second 0.2 micron filter. The actual concentration of nutrients in this water was empirically determined during the standardization calculations.
The concentrations (micro-mole per liter) of the working standards used were:

	uM N+N	uM PO4	uM SiO3	uM NO2
0)	0.0	0.0	0.0	0.0
1)	15.50	1.2	60	0.50
2)	31.00	2.4	120	1.00
3)	46.50	3.6	180	1.50

Analytical Problems
No major analytical problems were noted. No samples were lost.

(4) Oxygen
Although ULPGC group was responsible for the determination of dissolved oxygen, the SIO-ODF system was made available in order to compare methodologies. The ULPGC system is a potentiometric endpoint detection system whereas the SIO-ODF system uses a photometric endpoint detection based on the absorption of 365 nm wavelength UV light. Potassium iodate standards were swapped between the two groups and used to confirm the calibration concentration of the thiosulfate titrating solution. The results from both groups determined the concentration of thiosulfate to an error on the order of 0.03%, well within the precision of the instruments. On three stations (40, 42, and 66) dissolved oxygen was sampled and analyzed by both groups, each using their own calibrated glass bottles and thiosulfate titration solution. The results are plotted in section 3.1.3, figure 3.1.3.3. The results of the three stations indicate a standard deviation of ±0.43 μmol kg^{-1}, an error determination of less than 0.11%, well within the precision of the instruments. These results indicate both groups prepared their potassium iodate standard solution satisfactorily and that both systems are reliable for at-sea determination of dissolved oxygen concentration. Dissolved oxygen values reported for all stations, including SOCCOM stations, are from the ULPGC data.

(5) Alkalinity/pH
335 samples from SOCCOM CTD stations were taken for alkalinity/pH. Approximately 10% of samples were duplicates. Samples were drawn from the Niskin bottles, preserved with mercury (II) chloride and packed for shipping via air freight back to SIO (Andrew Dickson).

(6) HPLC and POC
36 near-surface samples from SOCCOM CTD stations were taken for HPLC analysis. 1-2L of sample was filtered in the dark through glass fiber filters. Filters were immediately stored in aluminium foil packages in a dewar of liquid nitrogen. 36 near-surface samples from SOCCOM CTD stations were also taken for POC analysis. 1-2L of sample was filtered in the dark through pre-combusted glass fiber filters. Filters were immediately stored in pre-combusted aluminium foil packages in a dewar of liquid nitrogen. At each station one set each of HPLC and POC samples was a duplicate. Samples were packed for shipping (dry shipper) via air freight back to University of Maine (Emmanuel Boss).

(7) Salinity
Salinity samples were collected at all depths from the SOCCOM CTD stations. Samples were analyzed by H. Zanowski using AWI's shipboard OPS system.

(8) Preliminary (expected) results

All floats reporting back to shore successfully. pH sensor malfunctioned on float 0508.

(9) Data management

SOCCOM will make all ODF nutrient analyses available immediately after collection and onboard quality control, for merging with the other data sets collected on the ship, whether they are collected at float locations or at other stations. We will make all pH/alkalinity data sets available after they are analyzed at SIO.

Rosette sample data for SOCCOM float calibration is being assembled and merged by Robert Key at Princeton U. CTD and fluorometer/transmissometer profile data for SOCCOM float calibration is being assembled by Sharon Escher at SIO.

For profiles at float locations, including all discrete rosette samples and CTD/fluorometer profiles: it is important that these data be available to us for calibration of the floats, in preliminary form and then later with quality control/calibration. SOCCOM can assist with discrete data merging. It would be highly preferable that the data from these stations be publicly available as soon as possible. SOCCOM would like to post these data on its own website as part of the float program (R. Key).

For datasets collected at other stations, where floats are not deployed, but where SIO ODF has performed nutrient analyses, it would be advantageous to us to have access to the profile data for quality control. For stations with full carbon measurements, it would be highly advantageous to collaborate with ULPGC and AWI to extend the SOCCOM empirical algorithm for carbon profiles based on the float data; the algorithm will be developed by SOCCOM (L. Juranek, Oregon State University; R. Feely, NOAA/PMEL). SOCCOM can assist with discrete data merging and quality control. Data release policy will be according to the Chief Scientist (O. Boebel).

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